Fast Semivolatiles Analysis using the Agilent Technologies 6890/5973 inert GC/MSD

Application

Environmental

Author

Mike Szelewski
Agilent Technologies, Inc.
2850 Centerville Road
Wilmington, DE 19808-1610
USA

Abstract

The analysis of semivolatiles presents challenges due to the simultaneous measurement of acids, bases, and neutrals over a wide concentration range. Due to productivity demands, laboratories want to run faster while maintaining linearity and sensitivity for even the most active compounds. The Agilent Technologies 6890/5973 inert gas chromatography/mass selective detector system is designed to meet the criteria for fast analysis, while minimizing activity and maintaining linearity.

Introduction

Semivolatiles analysis concurrently measures a mix of acids, bases, and neutrals. This mix presents a challenge for instrument design due to the interaction of the analytes with the instrument and consumables. Most laboratories analyze for 70–100 compounds with a chromatographic run time of 25–40 minutes. The calibration range required for the analysis varies dependent on a particular laboratory's statement of work. Historically a range of 20–160 ng was used. With the increased sensitivity of newer gas chromatography/mass spectrometry (GC/MS) systems, laboratories are moving toward lower minimum detection limits (MDLs) and pushing the calibration range down to 5 ng.

The Agilent 6890/5973 inert gas chromatograph/mass selective detector (GC/MSD) system was designed to meet the demand for these lower MDLs. A new uncoated solid source material has shown improved performance for the most active compounds, such as 2,4-dinitrophenol.

This inert source allows for less material injected onto the column while maintaining mass spectrometer performance. Split injections are possible where only splitless would suffice before. The ability to do split injections matches very well with smaller diameter columns such as 100 µm. These smaller columns provide for run times of 10 minutes or less.

This application note will show the performance of the Agilent 6890/5973 inert for semivolatiles using a 100-µm id column with a run time of 7.5 minutes and a calibration range of 5–200 ng.

Instrument Operating Parameters

The recommended instrument operating parameters are listed in Table 1. These are starting conditions and may have to be optimized.

Table 1. Gas Chromatograph and Mass Spectrometer Conditions

GC	Agilent Technologies 6890		
Inlet	150 psi EPC split/splitless		
Mode	Split, 1 µL injected		
Split ratio	10:1		
Inlet temp	250 °C		
Pressure	118 psi		
Split flow	22.8 mL/min		
Total flow	26.9 mL/min		
Gas saver	Off		
Inlet liner	Siltek™ Cyclosplitter, 4-mm id, Restek part number 20706-214.1		
Oven	240 V		
Oven ramp	°C/min	Next °C	Hold min
Initial		40	0.20
Ramp 1	45	320	1.58
Total run time	8.0 min		
Equilibration time	0.5 min		
Oven max temp	325 °C		
Column	Agilent Technologies HP-5MS Custom		
Length	12.5 m		
Diameter	100 µm		
Film thickness	0.1 µm		
Mode	Ramped flow		
Flow	mL/min[2]	mL/min	Hold min
Initial		2.3	0.10
Ramp 1	10	0.8	0.00
Inlet	Front		
Outlet	MSD		
Outlet pressure	Vacuum		
MSD	Agilent Technologies 5973 inert		
Solvent delay	0.95 min		
EM voltage	Run at DFTPP tune voltage = 1200 V		
Low mass	35 amu		
High mass	500 amu		
Threshold	0		
Sampling	1		
Scans/s	5.92		
Quad temp	150 °C		
Source temp	230 °C		
Transfer line temp	280 °C		
Repeller voltage	DFTPP tune value		
Emission current	DFTPP tune at 35 µamp, run at 25 µamp		

Calibration standards

Accustandard, New Haven, CT. Part number M-8270-IS-WL-0.25x to 10x, 77 compounds at eight concentration levels with six ISTDs at 40 ppm.

The Agilent 6890 with a 150 psi inlet (option) is necessary for both the initial high flow during injection and to maintain constant flow during the run. A 10:1 split is used to match the column capacity to the calibration concentration range. Higher splits can be used but splitting less or using splitless will cause peak overload and too much distortion for good integration.

The inlet liner was found to be of low activity, as it does not contain glass wool. Proper mixing for split injections is done by the internal liner geometry. This liner was also found to perform adequately for higher split ratios and for splitless.

The Agilent 6890 240 V oven was necessary for the 45 °C/min oven program ramp used.

The custom order HP-5MS column was obtained in a 20 m length and cut down to 12.5 m. The ramp flow allows for faster transfer of analytes onto the column to minimize exposure to the inlet liner. Ramp flows are easily set by the software and are accomplished with electronic pneumatic control (EPC).

The Agilent 5973 inert was tuned using the automatic DFTPP target tune, as required by some Government methods. After tuning, the emission current was manually set to 25 µamp. This was done to maximize linearity for easily ionized compounds. The sampling rate was changed from the default of 2 to 1, while preserving sufficient sensitivity. The resultant 5.92 scans/s yields a minimum of eight data points across the narrowest peaks.

Results

The system was calibrated at eight levels, 5, 10, 20, 50, 80, 120, 160, and 200 ppm. The total ion chromatogram (TIC) for the 5-ppm level is shown in Figure 1. Each calibration level contained 77 compounds together with six internal standards (ISTDs) at 40 ppm.

The relative response factor (RRF) was calculated automatically for each compound by the GC/MSD ChemStation software. Linearity was determined by calculating the percent relative standard deviation (%RSD) of the RRFs across the calibration range for each compound and was performed automatically by the software in conjunction with Microsoft® Excel.

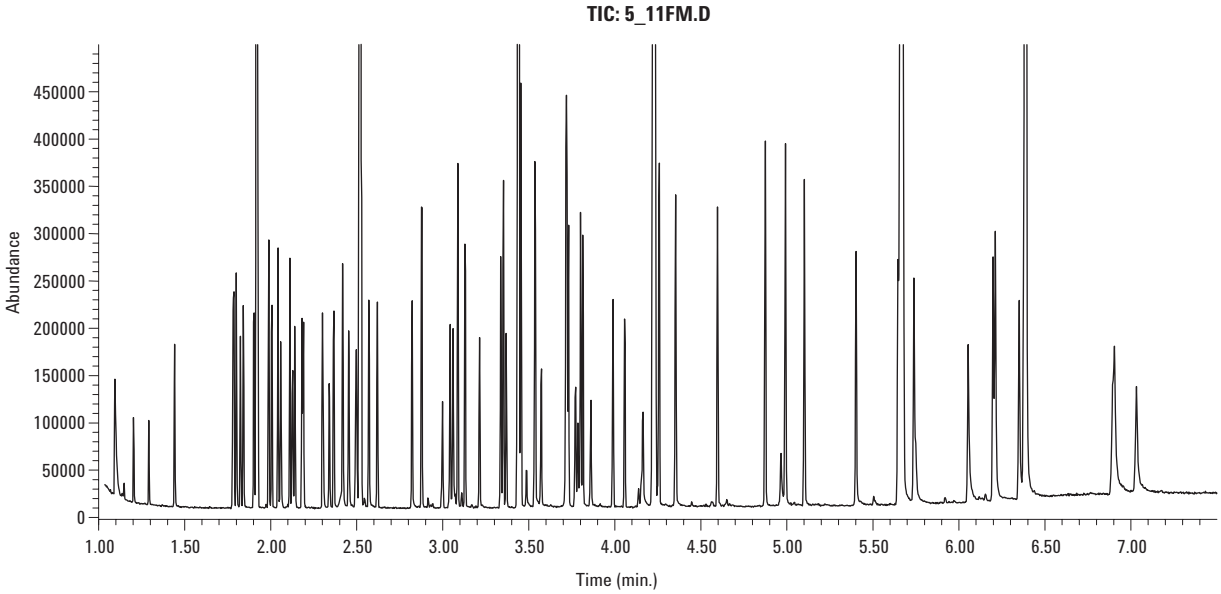

Figure 1. Five ppm each 77 semivolatiles and six ISTDs at 40 ppm each.

There are published Government Methods, such as USEPA Method 8270D for Semivolatiles, that specify criteria for suitable RRFs and %RSD. In Method 8270D, minimum system performance of four active compounds, the system performance check compounds (SPCCs) is measured by the average RRF.

Table 2 lists the Method 8270D SPCC criteria, and performance of the Agilent 5973 inert together with an Agilent 5973 system. The Agilent 5973 inert data exceeds the 8270D criteria. The Agilent 5973 inert also shows exceptional results compared to the Agilent 5973. These results are superior because they were run 10:1 split, putting 10× less compound on column than those run on the Agilent 5973.

Table 2. SPCCs, Comparison of Average RRF

	8270D Criteria	Agilent 5973 inert	Agilent 5973
Calibration range, ppm		0.5–20	5–160
N-Nitroso-di-n-propyl amine	0.050	1.146	0.970
Hexachlorocyclopentadiene	0.050	0.284	0.253
2,4-Dinitrophenol	0.050	0.188	0.075
4-Nitrophenol	0.050	0.236	0.162

Linearity is shown in Table 3. The 77 compounds were grouped as indicated. The RSDs of the RRFs were averaged to show performance for entire compound classes, not just a few selected analytes. The linearity of the Agilent 5973 inert is significantly better than the Agilent 5973 across the same concentration range and across an extended range.

Table 3. Average RSDs of RRFs by Compound Class

	Agilent 5973 inert	Agilent 5973 inert	Agilent 5973
Calibration range, ppm	0.5–20	2–16	20–160
Miscellaneous base neutrals (19)	8	5	11
Acids (17 phenols, dinitrophenols)	8	5	11
Bases (12)	8	6	12
Phthalates, ethers (13)	9	6	12
PAHs (16)	7	5	8

Conclusions

The Agilent 6890/5973 inert shows improved response for active compounds such as nitrophenols at low levels. This improved response gives better linearity across the calibration range. Split injections are now possible while maintaining sufficient response and fast analysis can be done using 100-µm columns. Analysis of 77 analytes and six ISTDs can be accomplished in less than 8 minutes over an extended calibration range of 0.5 ppm to 20 ppm.

For More Information

For more information on our products and services, visit our Web site at www.agilent.com/chem.

Printed in the USA
October 29, 2003
5989-0207EN